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(54) Title: PREBLEACHING OF PAPERPULP BEFORE A PEROXIDE BLEACHING STAGE (57) Abstract A method for bleaching paper making pulp with peroxide with enhanced efficiency for a chelating stage wherein the pulp after digestion, and possibly oxygen bleaching, is subjected to a mild chlorine dioxide treatment at acidic pH, an alkalization and a treatment with chelating agent at a high pH before a peroxide stage.		

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PREBLEACHING OF PAPERPULP BEFORE A PEROXIDE BLEACHING STAGE

The present invention relates to a method for bleaching paper making pulp with peroxide, comprising a treatment stage with chelating agents. More specifically, the invention relates to a method of improving the efficiency of a chelating stage according to which the pulp after digestion, and optionally oxygen bleaching, is subjected to a mild chlorine dioxide treatment at acidic pH, an alkalization and a treatment with a chelating agent before a peroxide stage.

Modern bleaching of paper making pulp has to be performed in an efficient way in order to keep the bleaching cost low while at the same time the strength and brightness shall be high. From environmental reasons the bleaching is performed with an increasing amount of oxygen and hydrogen peroxide which leads to a decreasing use of chlorine containing chemicals and therefore the discharge of chloroorganic pollutants decreases. During later years there has been a growing demand for bleaching methods that are easy to close, i.e. that it shall be possible to return filtrates obtained at the bleaching to the closed part of the pulp mill, completely or partly, in order to reduce the discharge of substances having a negative effect on the environment.

The resulting waste water from a bleach plant normally consists of alkaline and acidic filtrates which are discharged to the recipient, with or without preceding purification. In the normal case the acidic filtrate contains metal ions and transient metals from the wood and when the bleaching is performed with chlorine containing chemicals the filtrate also contains chloride ions. If chloride ions in larger amounts are returned to the closed part of the pulp mill without a purging mechanism this can lead to processing equipment on the problematic corrosion, which can be especially noticeable in the soda recovery unit in the manufacture of pulp according to the sulphate process. At the same time chlorine containing bleaching chemicals are very effective, and thus such a bleaching of paper making pulp can be made comparatively lenient and at reasonable bleaching costs.

From environmental reasons it is interesting to be able to reduce the use of chlorine containing chemicals in the pre-bleaching, since chloroorganic substances to a large extent are

formed in the prebleaching stage and since also the possibility of returning filtrate from the prebleaching stage is facilitated without the arise of the above discussed chloride problems.

5 It is well known per se to use a treatment of the pulp with a chelating agent (Q-stage) in order to eliminate disturbing ions of transient metals, especially manganese, and thereby to increase the efficiency in a subsequent peroxide bleaching stage (P-stage). Such a method has been developed and commercialized under the name Lignox of Eka Nobel AB, Sweden. A
10 treatment with chelating agents is normally made at a pH of 5 to 7 in order to give the best elimination of manganese. It is also known to treat pulp with a chelating agent in connection with a chlorine dioxide stage. The PCT application WO 96/06976
15 discloses a treatment with chelating agents directly before or after charging of chlorine dioxide without any intermediate wash with the object of being able to reduce the peroxide consumption and/or increase the brightness in the subsequent P-stage. The conditions in the Q- and D-stages in this method are
20 said to be normal and only general intervals are given for the pH and other parameters. Through the PCT application WO 95/27100 it is also known to treat pulp with chelating agents in connection with a chlorine dioxide stage and according to this application the treatment with chelating agent can be done
25 before, after or in the D-stage and preferably the treatment with chelating agents and the chlorine dioxide bleaching are performed in one and the same stage at a pH of 3 - 7.

The object of the present invention is to solve the problems discussed above and relates to a method of bleaching
30 paper making pulp at a highly closed prebleaching, comprising a pretreatment of the pulp with chlorine dioxide, followed by an alkalization and thereafter a treatment with chelating agents before washing directly followed by a peroxide bleaching stage. The method is more closely defined in the following claims.

35 According to the present method an introductory mild treatment with chlorine dioxide is performed, wherein the chlorine dioxide is added primarily with the object of preoxidizing the pulp so that metals disturbing the process, primarily transient metals and especially manganese, are more
40 exposed and can be bound more easily by chelating agents being

added in a subsequent stage before a peroxide bleaching stage. The addition of chlorine dioxide in the introductory treatment shall be so low that it does not cause noticeable problems in the recovery when the filtrate is returned. After that the
5 added chlorine dioxide has been consumed a pH increase is accomplished before the addition of a chelating agent. By this alkalization a disintegration of possible residual amounts of chlorine dioxide in the pulp into inactive substances is obtained. The alkalization also leads to that calcium is
10 attached to the pulp which is essential in order to prevent an accumulation of calcium in the closed part of the bleaching. An accumulation of calcium ions can namely lead to problematic deposits and incrust formation on the processing equipment. The bleaching in subsequent peroxide bleaching stages can, thanks
15 to the preceding treatment according to the invention, be made more efficient and result in a pulp with good strength. Further, the method is environmentally advantageous regarding the formation of chloroorganic substances and advantageous in view of corrosion and scaling in the processing equipment
20 without the need for costly purging methods, neither for calcium nor for chloride.

The method according to the present invention can be applied in bleaching of paper making pulp of softwood or hardwood type. The method can be applied for kraft as well as
25 sulphite pulp but is of greatest interest for kraft pulp in view of that this contains more calcium ions which can create problems.

After delignification and washing, in modern pulp mills the pulp is normally treated with oxygen and alkali in an oxygen
30 stage for further delignification, and dissolved wood substance is subsequently separated in a washing stage. The actual bleaching according to the present invention is subsequently started with a mild chlorine dioxide treatment wherein the amount of charged chlorine dioxide is maximum 15 kg, calculated
35 as kg active chlorine, per ton pulp. The chlorine dioxide charge should be low in order to eliminate the need of expensive purging processes for chloride when the filtrate is returned and the limit is hereby a return of maximum 2 - 3 kg chloride, calculated as kg Cl, per ton pulp. The chlorine
40 dioxide charge in the introductory treatment, the prebleaching,

lies thus advantageously within the interval from 2 to 15 kg/ton pulp and preferably within the interval from 5 to 10 kg/ton, where the chlorine dioxide is calculated as active chlorine. The chlorine dioxide charge depends to some extent on the preceding treatment of the pulp. If the pulp after digestion and washing has been oxygen delignified the amounts may lie in the lower part of the given intervals and in the upper part if it has not been treated with oxygen in a precedent stage. It can be noted that normal charges at prebleaching with chlorine dioxide is about 20 to about 40 kg/ton if the pulp is oxygen delignified and 40 to 70 kg/ton if the pulp has not been oxygen delignified. The prebleaching with chlorine dioxide is performed as is conventional at acidic pH, normally from 2 to 4. The temperature in the stage can be kept between about 40 and about 90°C and the stage can be performed at usual pulp consistencies of 8 to 16% and with residence times, which can be from 5 minutes to 1 hour.

After the chlorine dioxide treatment follows according to the present method an alkalization stage, which should be done to a pH of at least 8.5. The alkalization can suitably be done with NaOH. Suitably the alkalization is done to a pH of at least 9.5. The upper limit for the pH value is among other things determined by the risk of increased amount of re-deposited manganese on the pulp and suitably it does not exceed 11. The alkalization is, as mentioned above, important, partly in order to inactivate possible remaining amounts of chlorine dioxide in the pulp and chlorine dioxide deteriorates into chlorate and chlorite at high pH values, thereby no remaining chemical reacts with the chelating agent added later, and partly because calcium is redeposited on the pulp at higher pH values.

After the alkalization, a Q-stage is performed, i.e. a chelating stage, at said high pH value, minimum 8.5. The chelating agent will hereby keep ions of transient metals, primarily manganese, in solution while calcium deposits on the pulp, which, as already mentioned, is advantageous in order to prevent or reduce deposition of calcium salts which can lead to clogging of pipes and other equipment and reduced function of the process equipment.

As chelating agents can be used any such agent which binds

the actual disturbing trace metals, primarily manganese, copper and iron. Suitable chelating agents are aminocarboxylic acids, such as e.g. ethylenediaminetetra-acetic acid (EDTA), diethylenetriaminepenta-acetic acid (DTPA) and triethylene-tetraaminehexa-acetic acid (TTHA), aminophosphonic acids, such as e.g. ethylenediaminetetramethylene-phosphonic acid, phosphonic acids, such as e.g. hydroxyethyldi-phosphonic acids, and polyphosphates. In practice, usually EDTA or DTPA are used as chelating agent and in the present method DTPA is preferably used. The chelating stage is usually performed at elevated temperature, from about 40°C up to 95°C and the amount of chelating agent, calculated as pure product, should be at least 0.5 kg/ton pulp but can be to 5 kg/ton. Preferably it lies within the interval from 1 to 2 kg/ton. The pulp consistency in the chelating stage is not critical but can vary e.g. from 2 to 20 % by weight cellulose containing material. Suitably, however, the consistency lies within the interval from 8 to 16 % in order to suit conventional processing equipment. The treatment time in the Q-stage depends on among other things the temperature and should be at least 5 minutes and preferably at least 60 minutes and can if necessary be up to several hours.

The actual additions of the chemicals, chlorine dioxide, alkali and chelating agent, in the above described three stage treatment can e.g. be made in one or several mixers, pumps or dilution circulations. The three stages of pretreatment are performed in a sequence, without intermediate washing. The pulp treated according to the above is subsequently, after washing, transferred to a peroxide bleaching stage (P-stage), wherein usually hydrogen peroxide is used, even if, in principal, it is possible to use other peroxides. The P-stage can be performed in a conventional way, i.e. at alkaline pH, usually within the pH-interval 10 - 12, a temperature from about 50 to about 110°C and with a peroxide addition, hydrogen peroxide or a corresponding amount of another peroxide, which usually lies within the interval 5 to 50 kg/ton pulp. The peroxide stage can, if desired, be complemented with an oxygen addition and then suitably of at least 1 kg/ton pulp. The oxygen addition in this stage suitably amounts to maximum 20 kg/ton pulp and preferably to maximum 10 kg/ton pulp. The pulp consistency in the P-stage normally lies within the interval from 8 to 16 %.

After the P-stage the pulp is washed and is normally transferred to further bleaching stages, e.g. one or several chlorine dioxide stages or a further peroxide stage.

5 The method according to the present invention is well suited for use in a hardly closed bleaching plant wherein all precedent stages are alkaline. The filtrate from the P-stage can be returned through the pretreatment stage directly to the digester wash or to the wash of a subsequent oxygen stage.

Claims

1. A method for bleaching of paper making pulp, characterized in that the pulp, before a peroxide bleaching stage, is subjected to a prebleaching treatment in three stages without intermediate washes, whereby the pulp is first treated with chlorine dioxide in an amount of maximum 15 kg/ton, calculated as kg active chlorine per ton, at acidic pH, thereafter the pulp is made alkaline to a pH of minimum 8.5, and is then treated with a chelating agent at a pH of minimum 8.5, whereupon the pulp is washed.
2. A method according to claim 1, characterized in that the pulp is treated with chlorine dioxide in an amount of from 2 to 15 kg/ton.
3. A method according to claim 1 or 2, characterized in that the chlorine dioxide treatment is made at a pH not exceeding 4.
4. A method according to claim 1, characterized in that the alkalization is made to a pH of minimum 9.5.
5. A method according to claim 1, characterized in that diethylenetriaminepenta-acetic acid is added as chelating agent.
6. A method according to any of the preceding claims, characterized in that the addition of the three chemicals chlorine dioxide, alkali and chelating agent is made in one or several mixers, pumps or dilution circulations.
7. A method according to claim 1, characterized in that the peroxide bleaching stage is performed in the presence of oxygen.
8. A method according to any of the preceding claims, characterized in that the filtrate from the peroxide stage is returned through the pretreatment stage and thereafter to a preceding stage.
9. A method according to any of the preceding stages, characterized in that the pulp is a kraft pulp.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/01810

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/10, D21C 9/14, D21C 9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9606976 A1 (SUNDS DEFIBRATOR INDUSTRIES AB), 7 March 1996 (07.03.96), page 2, line 1 - line 20; page 4, figure 2, abstract --	1-9
A	WO 9625552 A1 (A.AHLSTROM CORPORATION), 22 August 1996 (22.08.96), page 11, line 1 - line 7; page 15, line 33 - line 35; page 16, line 3, figures 1,3, abstract --	1-9
A	WO 9527100 A1 (MO OCH DOMSJÖ AKTIEBOLAG), 12 October 1995 (12.10.95) -- -----	1-9

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Further documents are listed in the continuation of Box C.

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See patent family annex.

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Information on patent family members

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